60. *Electrophilic Substitution. Part VII.* Rates of Chlorination of Aromatic Hydrocarbons.*

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Rate constants have been measured for the chlorination of several polycyclic aromatic hydrocarbons in acetic acid. Kinetic measurements have also been made in a mixture of carbon tetrachloride and acetic acid. The results are compared with those for nitration and are discussed in terms of a molecular-orbital treatment.

LAUER and ODA[1] and de la Mare and Robertson[2] found the reactions of benzene and naphthalene with chlorine in acetic acid to be of the second order. The latter authors noted that the kinetics were complicated owing to slight autocatalysis by hydrogen chloride generated in the course of the reaction.

We have measured the rates of chlorination at 25° of benzene, diphenyl, naphthalene, phenanthrene, and triphenylene in acetic acid, and of diphenyl, naphthalene, phenanthrene, and pyrene in carbon tetrachloride–acetic acid (3 : 1 by volume). The reactions were of the second order. Excess of hydrocarbon was used in each experiment, and the rate constant, k_2, was obtained by application of the pseudo-first order equation :

$$k_2 = \frac{-2{\cdot}303}{[\mathrm{ArH}]_0}\frac{\log_{10}[\mathrm{Cl_2}]}{t} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (1)$$

where $[\mathrm{ArH}]_0$ is the initial hydrocarbon concentration and $\mathrm{Cl_2}]$ is the chlorine concentration at time, t. The quantity, $\log_{10} [\mathrm{Cl_2}]/t$, was obtained by plotting $\log_{10}$ (titre) against time. The straight-line graph showed the reaction to be of the first order with respect to the chlorine concentration, and repetition of the experiment with different hydrocarbon concentrations established the order with respect to the hydrocarbon concentration. Since the accuracy of the experiments was not high, the magnitude of the autocatalytic acceleration of the reaction could not be determined reliably, and the effect was, therefore, ignored. The rate of chlorination of a hydrocarbon was much faster (*ca.* 10^3) in acetic acid than in the carbon tetrachloride–acetic acid. Thus the chlorination of the most reactive hydrocarbon, pyrene, could not be followed in acetic acid, and benzene reacted too slowly for measurement in carbon tetrachloride–acetic acid. The results are summarised in the following tables; we consider the values given to be correct to within at most one unit in the last significant figure.

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* Part VI, *J.*, 1956, 3581.

[1] Lauer and Oda, *Ber.*, 1936, **69**, 1061.

[2] de la Mare and Robertson, *J.*, 1943, 279.

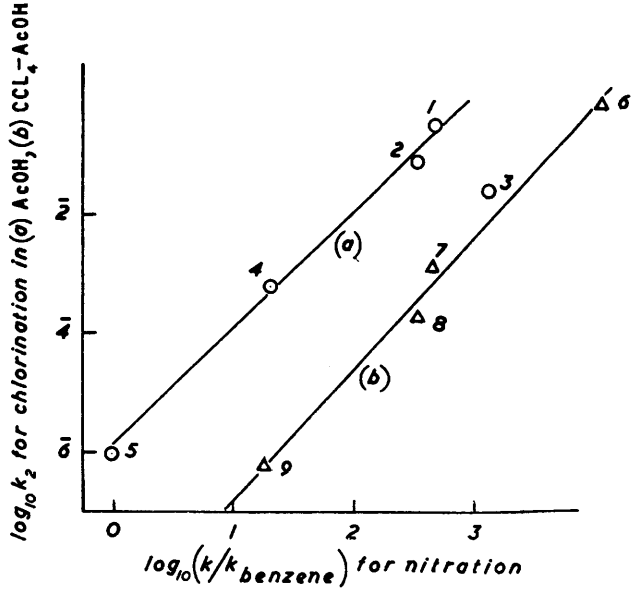
TABLE 1. *Chlorination in acetic acid.*

Hydrocarbon	[Hydrocarbon]	Initial [chlorine]	k_2 (l. mole^{-1} sec.$^{-1}$)
Benzene	6×10^{-1}	5×10^{-2}	6×10^{-7}
Diphenyl	2×10^{-1}	3×10^{-2}	$6{\cdot}9 \times 10^{-4}$
Naphthalene	3×10^{-2}	3×10^{-3}	$6{\cdot}3 \times 10^{-2}$
Phenanthrene	6×10^{-3}	10^{-3}	$2{\cdot}9 \times 10^{-1}$
Triphenylene	8×10^{-3}	10^{-3}	$2{\cdot}2 \times 10^{-2}$

TABLE 2. *Chlorination in carbon tetrachloride–acetic acid* (3 : 1 *by vol.*).

Hydrocarbon	[Hydrocarbon]	Initial [chlorine]	k_2 (l. mole^{-1} sec.$^{-1}$)
Diphenyl	8×10^{-1}	7×10^{-2}	9×10^{-7}
Naphthalene	3×10^{-1}	3×10^{-2}	$1{\cdot}9 \times 10^{-4}$
Phenanthrene	7×10^{-2}	8×10^{-3}	$1{\cdot}3 \times 10^{-3}$
Pyrene	10^{-2}	$1{\cdot}5 \times 10^{-3}$	$7{\cdot}1 \times 10^{-1}$

In Part VI[3] of this series it was shown that with few exceptions the partial rate factors for nitration of a number of polycyclic hydrocarbons were in accordance with the prediction of a simplified molecular-orbital treatment.[4, 5] The numerical value (—6·0 kcal./mole) of the empirical parameter,[3] β'_x, was however much smaller than the calculated value[6] of the carbon–carbon resonance integral. An explanation was put forward which implied that the magnitude of β'_x would depend on the nature of the substitution reaction.



1, *Phenanthrene.* 2, *Naphthalene.* 3, *Triphenylene.* 4, *Diphenyl.* 5, *Benzene.* 6, *Pyrene.* 7, *Phenanthrene.* 8, *Naphthalene.* 9, *Diphenyl.*

In the Figure the logarithms of the rate constants for chlorination in (*a*) acetic acid and (*b*) carbon tetrachloride–acetic acid (3 : 1) are plotted against the logarithms of the corresponding relative rates of nitration.[7] If we ignore differences in isomer distribution between the chlorination and nitration products (a necessary approximation, since the proportions of isomeric chlorination products are not known), then the gradients give the

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[3] Dewar, Mole, and Warford, *J.*, 1956, 3581.

[4] Dewar, *J. Amer. Chem. Soc.*, 1952, **74**, 3341.

[5] Bavin and Dewar, *J.*, 1956, 164.

[6] Wheland, *J. Amer. Chem. Soc.*, 1941, **63**, 2025.

[7] Dewar, Mole, and Warford, *J.*, 1956, 3576.

ratios $\beta_{\text{chlorination}}/\beta_{\text{nitration}}$ for the two chlorination media. Taking the value, $\beta_{\text{nitration}} = -6{\cdot}0$ kcal./mole, we thus derive :

$$\beta \text{ for chlorination in acetic acid} = -11 \text{ kcal./mole} \quad . \quad (2)$$

$$\beta \text{ for chlorination in carbon tetrachloride–acetic acid } (3:1) = -13 \text{ kcal./mole} \quad . \quad (3)$$

These values demonstrate not only the variation of β'_x with the substituting agent, but also the dependence of β'_x for chlorination on the medium. Since for any hydrocarbon k in acetic acid $\gg k$ in carbon tetrachloride–acetic acid, the above figures confirm the rule quoted in Part VI [3] that the more reactive is a substituting agent, X, the lower is the numerical value of β'_x and the less orientational selectivity the reagent should show. In the case of toluene, chlorination in acetic acid has been found to be much more selective than nitration (see Brown and Nelson [8,9]).

The point for triphenylene lies well off line (*a*) in the Figure. Triphenylene was found to be about four times as reactive towards nitration as required by theory.[3] It seems that no such anomalously high reactivity is shown in chlorination.

EXPERIMENTAL

Materials.—The hydrocarbons used were as described earlier.[7,10,11] Portions of the same batch of " AnalaR " acetic acid and of the same mixture of " AnalaR " carbon tetrachloride and " AnalaR " acetic acid were used as solvents for the respective sets of experiments.

Kinetic Measurements.—The reaction was started by adding an approximately N/3-solution of chlorine in the appropriate solvent (1—50 ml.) to a solution of hydrocarbon in the same solvent in a thermostat at 25°. The total volume of solution was *ca.* 100 ml. Most reactions were followed as far as the third half-life by pipetting 5-ml. samples of the mixture into excess of 10% potassium iodide solution (10 ml.) and titrating against sodium thiosulphate solution (0·1M—0·01M). In the slower reactions (benzene in acetic acid, and diphenyl in carbon tetrachloride–acetic acid) high concentrations of chlorine were used, and, to avoid loss of chlorine due to volatility, samples (5 ml.) of reaction mixture were sealed in tubes of *ca.* 7 ml. capacity. Tubes were opened at intervals of 1—2 days and the residual chlorine was determined as above. These reactions were followed only as far as the first half-life.

Blank experiments were carried out in all cases to determine whether chlorine was lost other than by reaction with the hydrocarbons. The loss was negligible except for the very slow chlorination of benzene in acetic acid; here a correction was made in calculating the rate constant.

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[8] Brown and Nelson, *J. Amer. Chem. Soc.*, 1953, **75**, 6292; 1955, **77**, 2300 *et seq.*

[9] Brown, *J. Org. Chem.*, 1956, **21**, 145.

[10] Dewar and Mole, *J.*, 1956, 1441.

[11] Dewar, Mole, Urch, and Warford, *J.*, 1956, 3572.